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The goal of the High Energy Densiry Matter Program of the Air Force, the development of a rocket propellant that significantly improves on the performance of the conventional liquid hydrogen/liquid oxygen rocket propellant, is an ambitious and important undertaking. The "next generation" propellant must be energetic, economical, and safe from both an engineering and environmental standpoint. These properties are often mutually exclusive and a balance of availability and ease of use must be struck. Cryogenic solids, specifically "energized" solid hydrogen and/or solid oxygen, have been an area of study for years. Using cryogenic solids, the increase in density gives rise to a modest increase in theoretical performance, but more importantly, cryogenic solids provide a low-temperature environmentrequired for the stable trapping of energetic species. Obtaining large concentrations of energetic species even in this low temperature environment has proven difficult. One system where ton quantiites of the reactant species can be manufactured is a system using a mixture of solid ozone/oxygen; this mixture is the focus of the research on this project.

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# ENERGETIC SPECIES IN CONDENSED OXYGEN/OZONE

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#### **ABSTRACT**

The goal of the High Energy Density Matter Program of the Air Force, the development of a rocket propellant that significantly improves on the performance of the conventional liquid hydrogen/liquid oxygen rocket propellant, is an ambitious and important undertaking. The "next generation" propellant must be energetic, economical, and safe from both an engineering and environmental standpoint. These properties are often mutually exclusive and a balance of availability and ease of use must be struck. Cryogenic solids, specifically "energized" solid hydrogen and/or solid oxygen, have been an area of study for years. Using cryogenic solids, the increase in density gives rise to a modest increase in theoretical performance, but more importantly, cryogenic solids provide a low-temperature environment required for the stable trapping of energetic species. Obtaining large concentrations of energetic species even in this low temperature environment has proven difficult. One system where ton quantities of the reactant species can be manufactured is a system using a mixture of solid ozone/oxygen; this mixture is the focus of the research on this project.

### CONTENTS

ABSTRACT	i
INTRODUCTION	1
BACKGROUND	2
Solid Oxygen	2
Solid Ozone	3
Solid Oxygen/Ozone Mixtures	3
Solid Ozone Detonation	4
RESULTS OF WORK	4
Apparatus Construction and Capabilities	5
Using Infrared O <sub>2</sub> Absorptions as a Monitor of Crystal Structure	6
Wavelength Dependence of O <sub>x</sub> Production in Solid O <sub>2</sub>	6
O•••O <sub>3</sub> Complex or Unstable Site for O <sub>3</sub> ?	10
Picosecond Experiment and Dimer Specific Dissociation	11
Publications and Presentations	13
REFERENCES	15

#### INTRODUCTION

Research performed in the High Energy Density Matter (HEDM) program over the past years indicates that a promising approach to generating novel propellants with high specific impulse (I<sub>sp</sub>) is that of cryogenic fuels in which energetic species are incorporated. Two factors point to the advantages of using cryogenic solids. For one, the density increase always gives rise to a modest increase in the specific impulse, but more important, cryogenic solids provide the low-temperature environment required for the stable trapping of energetic species. Because a liquid hydrogen and liquid oxygen propulsion engine is the system to which all new concepts must be compared, the initial logical step is to investigate solid hydrogen or solid oxygen with some additive stored in these solids to enhance performance.

Detailed consideration has been given to storing fuel additives in solid hydrogen, but given the experimental and system difficulties with this concept, any real world system employing solid hydrogen seems many years in the future. Solid oxygen with liquid hydrogen as a fuel has less practical problems and the replacement of some or all of the oxygen by ozone would lead to a significant boost in I<sub>sp</sub>. In principle, the solid oxygen/ozone oxidant can be kept cold by the liquid hydrogen fuel, making any future engine design less complex. The difficulty in storing large quantities of ozone safely has, thus far, suppressed large-scale experimental realization and testing of the oxygen/ozone concept. However, this practical storage problem must be addressed now.

The potential advantages of the oxygen/ozone solid system appear to justify examining the handling problems. The prime advantage of this system is that ton quantities of all the components can be produced with existing technologies. Many other proposed HEDM materials can be generated in milligram or in gram quantities, but production scale-up is a difficult process and may be extremely expensive. In the oxygen/ozone solid system, oxygen/ozone mixtures can be produced from inexpensive raw materials (i.e., oxygen from air) and in quantities far beyond the wildest dreams of the manufacturers of other HEDM materials.

Recently, a hydrogen and solid oxygen motor was tested at the United States Air Force Phillips Laboratory with promising results [Rice, 1996]. The next logical step is to add ozone in significant quantities (> 10%) to the solid oxygen, but how can this be done safely? Understanding the properties of the oxygen/ozone mixtures will be extremely important in making this next step toward the real-world rocket engines. Safe handling of such large quantities will be crucial and establishing a reliable technique for engineering fuel will be highly challenging. This next step must be accomplished soon.

The safe handling of ozone and oxygen/ozone mixtures is such an important issue that it must be studied from different perspectives. For early success, both basic science studies and more applied investigations should be undertaken simultaneously. The intrinsic handling problems with the system can be addressed with the applied studies, but the underlying cause of these problems cannot be understood without the basic studies. We are investigating the basic science aspects of what happens in the oxygen/ozone system (i.e., how reactions proceed and how reactant species move in the solid).

These studies are evolving to more applied investigations addressing fabrication of an oxygen/ozone mixture with reduced shock sensitivity via multilayer deposition and/or the use of reaction inhibitors. What we are learning in the more basic investigation will be applied to the practical aspects of creating an oxygen/ozone solid that is significantly more stable than what has been achieved previously. The ultimate goal of this project is to develop a new technology to generate large quantities of highly energized oxygen fuel. Our approach is stepwise: developing a methodology; creating larger samples; and in then designing realistic test devices that we will use to perform preliminary tests on these oxygen/ozone mixtures.

#### BACKGROUND

Extensive literature exists on the properties of solid oxygen and, to a lesser extent, studies have been performed on solid ozone. Mixtures of the two species in cryogenic solids are less well studied. Before describing our work in this area, we summarize briefly what is known about oxygen, ozone, mixtures of both, and the detonation properties of ozone.

#### Solid Oxygen

Solid oxygen has magnetic and molecular properties that have been studied in detail using electrical, mechanical [Bates and Altshuler, 1995], and spectroscopic techniques [e.g., Ruoff and Desgreniers, 1991]. Here we describe the general features, highlighting significant facts, in order to understand the details given later. At low temperature and pressures near one atmosphere, three phases of the solid are observed,  $\alpha$ ,  $\beta$ , and  $\gamma$  [Etters et al., 1983]. The high temperature  $\gamma$ -phase is stable from the melting point (~ 55 K) to 43.8 K, where it transforms to the  $\beta$ -phase and is not observed in matrices due to its high vapor pressure. The rhombohedral  $\beta$ -phase converts to the  $\alpha$ -phase at 23.9 K. The  $\alpha$ -phase is monoclinic and the transition from  $\beta$  to  $\alpha$  is driven by strain, induced through magnetic interactions with only a small heat of transition.

We have examined this phase transition using the infrared line position of seeded ozone in O<sub>2</sub> as a marker. Using this frequency shift method, we observed a hysteresis effect in the phase

transition [Bressler and Copeland, 1997] similar to that recently observed using heat capacity measurements [Lipinski et al., 1996]. The Raman [e.g., Löwen et al. 1990], infrared [Cairns and Pimentel, 1965; Jones et al., 1985; Jodl et al., 1987], visible [e.g., Landau et al., 1962], and ultraviolet spectroscopy [Danilychev and Apkarian, 1995] is well-known. The infrared spectroscopy of solid oxygen samples was exploited for examining the quality of each matrix sample as described below.

#### Solid Ozone

Solid ozone has been thoroughly investigated by Wight and coworkers [Sedlacek and Wight, 1988; Wight, 1992; 1994]. Solid ozone can be decomposed to  $O_2$  via UV photolysis within the Harrley continuum. Photodestruction and photoabsorption cross sections at 308 nm have been measured and a photodestruction quantum yield of ~2 extracted [Sedlacek and Wight, 1988; Benderski and Wight, 1994; 1996], which is significantly lower than the gas phase value of 6 [Lissi and Heicklen, 1972]. Further investigations [Wight, 1992; 1994; Brosset et al., 1993] showed that the infrared absorptions of ozone alter severely as a function of deposition rate and temperature, due to gradual changes from a crystalline to an amorphous structure. This important observation will be explored and examined further in our construction of layered structures of  $O_3$  and  $O_2$  mixtures.

#### Solid Oxygen/Ozone Mixtures

Studies of elementary photodissociation processes of O<sub>3</sub> in O<sub>2</sub> are complicated by the large reactivity of the host material with O-atom fragments generated in the decomposition. However, investigations on mixtures of ozone in rare-gas solids have yielded an understanding of the preferred trapping sites [Brosset et al., 1993], the initial O<sub>3</sub> photodissociation process with permanent exit of the hot O fragment out of the rare-gas cage, and a description of thermal diffusion of O atoms through the rare-gas lattice [Benderski and Wight, 1996]. In contrast, little is known about mixed solid ozone/oxygen systems.

A recent study [Schriver-Mazzuoli et al., 1995] proposed photogeneration and stabilization of a novel, weakly bound O···O<sub>3</sub> complex isolated in solid oxygen, but our own studies had to eliminate this assignment. The Schriver-Mazzuoli study undertook isotopic studies on oxygen/ozone mixtures. However, the chosen combination of isotopically fully scrambled ozone in solid oxygen does not allow the detailed distinctions of fundamental molecular reaction steps undertaken in our own research. To our knowledge, there is no systematic study of the concentration dependence of the ozone reaction sensitivity in solid oxygen. Our work over the past few years has focused on

ozone/oxygen mixtures where ozone is a minor species. In the future work, we will significantly increase the ozone fraction in the oxygen.

#### Solid Ozone Detonation

unexpectedly and easily. This reputation is well-deserved, but very difficult to study in a systematic way. In one of the few systematic and well-designed investigations, the sensitivity of neat solid ozone toward laser-induced detonation was studied by Wight [Wight, 1992; 1994]. A critical film thickness of about 1 mm was determined, above which laser ignition with 266 nm light results in a violent chain reaction decomposing the entire layer [Wight, 1994]. Wight and coworkers found that this dangerous sensitivity can be significantly reduced by growing amorphous ozone structures. Thin ozone layers of approximately 0.1-mm thickness have proven their insensitivity toward exothermic decomposition regardless of sample structure (crystalline or amorphous) [Wight, 1994]; yet the largest grown crystals have thicknesses only on the millimeter scale. To date, nothing is known about the mechanical shock sensitivity of solid ozone at very low temperatures. A logical approach is to increase stepwise the ozone amount and to simultaneously shock test it. To our knowledge, solid mixtures with O<sub>2</sub> and layer structures of O<sub>2</sub> and O<sub>3</sub> have never been investigated. A key question is how to produce these layer structures and to determine how these layers reduce the shock sensitivity.

#### RESULTS OF WORK

During the past three years of the current project entitled, "Energetic Species in Condensed Oxygen", we have made significant advances in the study of O<sub>2</sub>/O<sub>3</sub> solids. We have

- Used nanosecond tunable ultraviolet laser light between 210 and 240 nm to generate previously unobserved, specifically oriented, ozone dimers in solid oxygen with irradiation.
- Used O<sub>2</sub> infrared absorptions as a sensor for the characterization of solid O<sub>2</sub> matrices,
   specifically for detecting defect sites and their healing during annealing.
- Used the line positions and intensities of ozone infrared absorptions to monitor the
  temperature of the thin O<sub>2</sub> crystal, even its small increase due to laser radiation
  heating, to examine the α-β phase transition in solid O<sub>2</sub>, and to determine the thermal
  stability of O<sub>3</sub> in specific sites and configurations in the O<sub>2</sub> host.

- Shown (via extensive investigation) that the previously observed infrared absorption assigned to an O···O<sub>3</sub> complex is due to an O<sub>3</sub> monomer in an unstable site.
- Grown macroscopic O<sub>2</sub> solid samples (0.5 cm × 0.5 cm × 0.5 cm) using magnetic fields to improve the optical quality, and examined these large crystals with both picosecond and nanosecond light in absorption and emission.
- Irradiated O<sub>2</sub>/O<sub>3</sub> matrices with visible picosecond laser light to selectively dissociate O<sub>3</sub> dimers generating O<sub>3</sub> monomers in unstable sites without perturbing the number of the other ozone monomers in the sample.
- Exploited isotopic substitution and isotopically segregated layered structures to examine the detailed photoinduced reaction pathways in the solid mixtures, thereby beginning an investigation into the photomobility of O atoms in solid oxygen.

All these studies help us understand the fundamental processes that occur in these HEDM materials. A key component of this investigation was the interaction of the matrices with tunable laser light in both the nanosecond and picosecond time domains. To our knowledge, these are the first studies investigating possible processes triggered by ultrashort pulses. Describing these results here in detail is not practical, but in the following sections we present key results on some of these topics. Reports and papers detailing our investigations are given in the appendices.

The experimental philosophy of this investigation was to start with solid oxygen and study its interaction with light at all wavelengths, then systematically increase the complexity by introducing ozone and other species in the oxygen system. To increase the quantities toward more realistic values, we investigated and established a fabrication process for free-standing oxygen crystals, allowing use of our spectroscopic tools in the entire UV to IR region. We must learn more about the properties of these solids and their mixtures on different size scales to truly understand solid oxygen and solid ozone as potential fuel candidates.

## Apparatus Construction and Capabilities

On this project, we built an apparatus for creating both oxygen free-standing crystals and oxygen matrices. We interfaced this cryogenic crystal growth chamber with the tunable nanosecond and picosecond laser systems from our laboratory. Using these facilities, we incorporated both photogenerated and seeded-ozone into the oxygen matrices. Matrices were also

briefly studied with other potential fuels additives, such as N<sub>2</sub>O. Figure 1 is a picture of the apparatus for generating a free-standing crystal of oxygen. The solid oxygen is seen inside the cuvette. After its growth, the cuvette is raised to give optical access to the crystal from the IR to the UV. Growing crystals with good reproducible optical quality over this entire spectral region was the focus of several investigations and, in summary, we discovered that slow condensation from the liquid in the presence of a strong magnetic field creates the most uniform samples with excellent optical transparency.

The apparatus was designed to be a versatile system that could switch between free-standing crystals to matrices. The majority of the experiments described below were performed on matrices deposited on a gold mirror mounted on the cryostat. Figure 2 shows a schematic of the experimental setup and the system for multilayer species generation.

# Using Infrared O2 Absorptions as a Monitor of Crystal Structure

One goal of our experimental program was to develop a method to characterize the cryogenic O<sub>2</sub> samples and to develop reliable and reproducible procedures for their production. These procedures can eventually be applied to more engineering oriented applications where methods to monitor the status of solid fuels in real rocket engine systems will be desired. Infrared methods are often the most useful tools for this purpose. However, generally, solid O<sub>2</sub> does not have an infrared absorption. Upon examination of the literature, one finds that O<sub>2</sub> shows an infrared absorption near 1550 cm<sup>-1</sup> due to crystal imperfections and nearby located defect sites [Cairns and Pimentel, 1965; Jones et al., 1985; Jodl et al., 1987].

We have exploited this property for the characterization of the quality of both free-standing crystals and thin-film matrices. This absorption feature is used to ensure reproducible systems from experiment to experiment. After rapid deposition from the gas phase to a cold (~15 K) gold-coated mirror, we see a strong absorption near 1552 cm<sup>-1</sup>, occasionally accompanied by three resolvable features at 1549, 1548, and 1546 cm<sup>-1</sup>, due to imperfections. When we anneal the crystals up to 25 K, these O<sub>2</sub> absorptions disappear permanently, indicating a successful (partial) healing of the defects. This is the sample we use for our irradiation studies. We also discovered the same absorptions disappeared permanently when cold matrices at 15 K were treated with 532 nm picosecond light of moderate intensity.

# Wavelength Dependence of Or Production in Solid O2

Using broad-band UV light from a medium pressure mercury are lamp, Schriver-Mazzuoli et al. [1995] showed that photodissociation of solid oxygen with  $\lambda > 245$  nm produces two

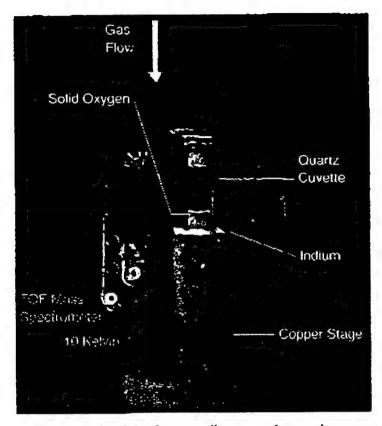


Figure 1. Photograph of the free standing crystal growth apparatus.

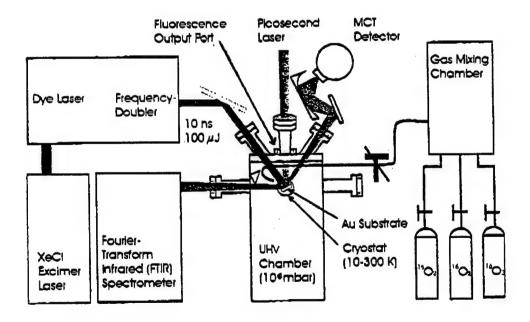


Figure 2. Schematic diagram of the thin film growth apparatus including the optical beam paths.

infrared features in the  $v_3$  band region of ozone. They claimed that only the higher frequency feature at 1037.8 cm<sup>-1</sup> is observed in ozone-doped oxygen matrices, and is thus assigned to matrix isolated  $O_3$ . For the other feature at 1030.9 cm<sup>-1</sup>, they performed calculations on ozone and attributed it to a weakly bound complex  $O_3$ . [Schriver-Mazzuoli *et al.*, 1995] isolated in the  $O_2$  matrix.

Our experiments on the origin of this feature are described below. We chose to examine  $O_x$  production in a more systematic manner using monochromatic pulsed laser light over the wavelength range from 210 to 260 nm. Figure 3 shows the absorption spectra in the  $v_3$  band region obtained following irradiation with specific wavelengths until no further changes in intensity were observed. An increased absorption for these features (going from 244 nm down to 210 nm) indicated a concentration increase by over a factor of 50. This increase is in accord with expectations about the decreasing ozone photodissociation cross section (in the Hartley-continuum) and the increasing  $O_2$  photodissociation cross section (in the Herzberg-continuum) over this wavelength range. More surprisingly, five new features in the  $v_3$  vicinity were observed, which do not show up when the laser wavelength is kept above 240 nm (below the  $O_2$  dissociation limit) or when  $O_3$ -doped  $O_2$  mixtures are deposited.

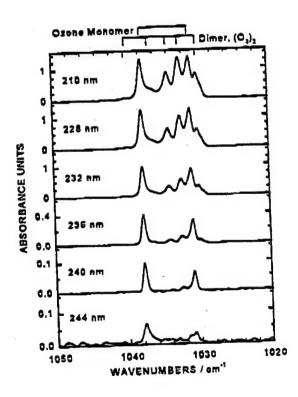


Figure 3. Wavelength dependent photogeneration of ozone monomers and dimers in neat oxygen matrices.

A detailed analysis of the formation kinetics led us to an initial understanding of these five new features. These bands grow in directly with a linear slope for small UV doses and level off for large doses according to a single exponential growth curve. The photodissociation of  $O_2$  in solid oxygen above the dissociation limit yields two  $O(^3P)$  atoms, which each react with one of the cage molecules to form  $O_3$ . Because both newly-formed ozone molecules share the same vacancy of the precursor  $O_2$ , they can rearrange to form a dimer  $(O_3)_2$ . This is experimentally evident from the interesting fact that, for small irradiation doses and  $\lambda \le 240$  nm, neither is the  $O_3$  monomeric vibration present in the IR spectrum nor is the controversial  $O \cdots O_3$  band present at 1030.9 cm<sup>-1</sup> [Bressler et al., (1997a)]. However, for prolonged irradiation, both features grow in the spectrum, exhibiting an S-shaped growth curve.

We explain the S-shaped growth curve in this way. The first-formed  $(O_3)_2$  will be dissociated in the corresponding Hartley continuum of a single  $O_3$  of the dirner, and the released  $O(^1D)$  atom eventually will react with an  $O_2$  to form  $O_3$  again. But this time one of the precursor  $O_3$  from the dirner has turned into a ground-state  $O_2$ , which thus may separate both  $O_3$  molecules from the dirner by one lattice constant, converting the precursor dirner into two isolated monomers. Hence, the experimental absence of monomeric ozone absorptions for small irradiation doses proves the absence of monomers for small UV doses, while the other new bands are due to  $(O_3)_2$  complexes. Concentration studies of ozone-doped oxygen matrices reveal one dominant dirner band at  $1039.9 \text{ cm}^{-1}$  and two weaker ones at  $1034.6 \text{ cm}^{-1}$  and  $1044.9 \text{ cm}^{-1}$ , in addition to some even weaker features attributed to aggregates in the  $1040-1050 \text{ cm}^{-1}$  region. Except for the band at  $1039.9 \text{ cm}^{-1}$  and possibly the one at  $1034.6 \text{ cm}^{-1}$ , none of the assigned dirner bands coincide with our photogenerated features in the  $1030-1040 \text{ cm}^{-1}$  region. This emphasizes the special configuration of our new species, which is not likely to be populated via gas-phase condensation.

The temporal stability of these dimeric (and monomeric) species is highly attractive. Even a one-week-old energized oxygen crystal maintained at 15 K in our laboratory showed no measurable loss in concentration as determined via their IR intensities. Even more exciting is the fact that the different spectral positions of these new dimeric absorptions correspond to different orientations of the (O<sub>3</sub>)<sub>2</sub> relative to each other and/or to the surrounding cage formed by O<sub>2</sub> molecules. Our engineering of different ozone dimers in solid oxygen [Bressler et al., 1997] was not achieved in previous studies of ozone-doped oxygen matrices.

Clearly, runable ultraviolet light is useful for creating ozone species with specific orientations. Whether the next step can be taken to initiate specific reactions with these oriented species is still under investigation.

# O···O<sub>3</sub> Complex or Unstable Site for O<sub>3</sub>?

As mentioned above, a manuscript appeared in the 1995 Journal of Chemical Physics claiming that certain infrared absorptions observed in the  $v_1$ ,  $v_2$ , and  $v_3$  regions of  $O_3$ , following irradiation of an oxygen matrix with UV light of a wavelength greater than 245 nm, could be assigned to a complex with an oxygen atom weakly bound to an ozone molecule,  $O - O_3$ . Confirming the existence of such a complex is important for this project because it could be a method to stabilize oxygen atoms in an  $O_2$  matrix or serve as a precursor reactant species so that a cyclic  $O_4$  could be produced. Because of these potential applications, we began an investigation to find ways to prepare more of this species, to examine its temperature properties and stability, and finally to confirm its existence. As described above, we used tunable ultraviolet laser light to study the wavelength dependence of its formation. We found, as we applied shorter wavelengths, that we could increase the concentration of the species. We learned, as described above, about the complexity of the formation of this and the other new dimer species.

We next studied the temperature dependence of the stability of the proposed O···O<sub>3</sub> complex and found that it remained stable throughout the  $\alpha$ -phase (T < 23.9 K), though it disappeared in the  $\beta$ -phase with increasing rates when the temperature was increased further. Its absorption shifted smoothly through both crystal phases to higher energy as the sample was heated, and the absorption disappeared irreversibly within minutes at 27 K. This temperature shift is opposite to that observed for the isolated O<sub>3</sub> band, which shows a shift to lower energy as the sample is heated and a pronounced 0.3 cm<sup>-1</sup> jump right at the  $\alpha$ - $\beta$  phase transition, as shown in the top of Figure 4. All of these properties observed to that point would be consistent with either those of the published complex or with an ozone monomer or dimer in an unstable site. We eliminated the possibility of it being an ozone molecule in a defect site by varying the number of defect sites in the sample and finding no difference in the production when a sample with a significantly larger number of defect sites is used.

In the key experiment, we succeeded in observing an absorption feature at the very same energy as the photogenerated one when we deposited dilute ozone/oxygen mixtures (1:10000). Rapid condensation on cold surfaces (14 K) was found to be optimal for observing the 1030.9 cm<sup>-1</sup> feature, though with very small intensity relative to the monomer band at 1037.8 cm<sup>-1</sup>. The blue shift of this feature with increasing temperature in the O<sub>3</sub>-seeded O<sub>2</sub> matrices and its rapid decomposition around 27 K, together with the simultaneous appearance of the dimer band at 1039.9 cm<sup>-1</sup>, is identical to the behavior of the photogenerated band and, thus,

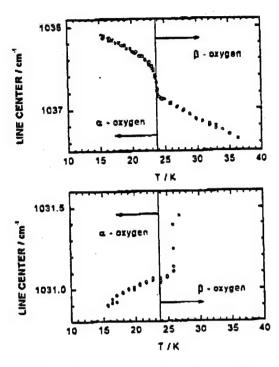


Figure 4. Temperature dependence of the line position of both ozone monomer absorptions in the  $v_3$  antisymmetric stretch region of  $O_3$ .

must be of the same origin, as shown in Figure 5. The absence of O atoms in the seeded sample was even further ensured by turning off the ionization gauge inside the sample chamber during deposition. The influence of ionization gauges on deposits is well-known, although often disregarded. We have observed both ozone monomer features after deposition of neat oxygen without a photolysis source due to the ion gauge breaking up O<sub>2</sub>.

Putting all this information together, we conclude that the previous assignment of the absorption to the O···O<sub>3</sub> complex is incorrect and confirmed that it is a monomer in an unstable site. The failure of Schriver-Mazzuoli et al. [1995] to observe this feature in vapor-deposited matrices can be explained quite naturally after these investigations. Deposition of ozone/oxygen mixtures at 20 K or higher, as they stated to be a typical procedure, is obviously too high to stabilize the monomer in an unstable site, and thus they did not observe it in their seeded crystals.

# Picosecond Experiment and Dimer Specific Dissociation

The majority of the experiments were performed with nanosecond laser pulses, but we observed other interesting phenomena with picosecond pulsed light at 532 nm. Irradiating O<sub>3</sub>-doped O<sub>2</sub> matrices with visible 100-ps laser light, we observe the selective photodissociation of

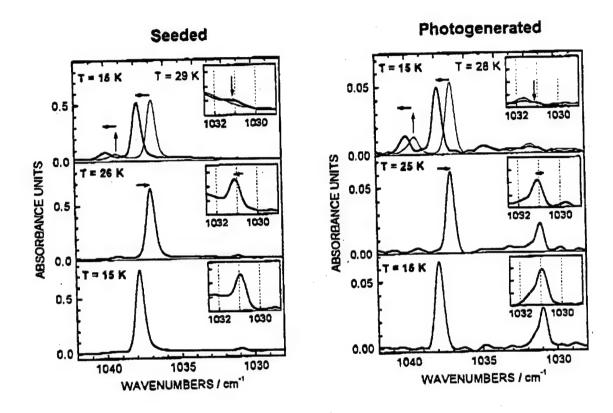


Figure 5. Identification of the proposed O···O<sub>3</sub> complex being an O<sub>3</sub> monomer in an unstable site via comparison of thermal behavior of the IR spectra of O<sub>3</sub> doped O<sub>2</sub> matrices with no photolysis source ("seeded", left) and of neat O<sub>2</sub> after irradiation with  $\lambda = 240$  nm ("photogenerated", right).

Bottom spectra: After preparation at T=15 K. Middle spectra: during heating (left: T=26 K, right: T=25 K). Top spectra: during T=29 K (left) and T=28 K (right), and after recooling to T=15 K. Arrows indicate changes relative to the previous spectra.

 $O_3$  dimers into ozone monomers. Figure 6 shows this phenomenon. We can enhance the production of the ozone monomer in the unstable site, and the increase in that absorption seems to be correlated with a decrease in dimer formation that has been correlated with that site. Experiments are still underway to see if this change is unique to the picosecond laser light or would also be observed with pulses of longer duration. Itradiation of matrices with picosecond light at  $1.06 \mu$  has resulted in severe heating of the sample due either to absorption by  $O_2$  or to the higher intrinsic power of the laser at that wavelength.

#### Publications and Presentations

The following publications have been or are being written acknowledging support through the current HEDM contract.

- 1. M. J. Dyer, C. G. Bressler, and R. A. Copeland, "Photodissociation of Solid Oxygen with Tunable Ultraviolet Laser Light: Ozone Production Monitored via Fourier Transform Infrared Spectroscopy," Chem. Phys. Lett. 266, 548-553 (1997).
- 2. C. G. Bressler and R. A. Copeland, "Temperature Effects on the Spectral Line Positions and Stability of Ozone Monomers and Dimers in Oxygen Matrices," in preparation.
- 3. C. G. Bressler, M. J. Dyer, and R. A. Copeland, "Photochemical Studies of Ozone in Oxygen Matrices," in preparation.
- 4. C. G. Bressler, B. T. Schwartz, and R. A. Copeland, "Using Low Temperature Matrices to Study Reactions of the O<sub>2</sub> Herzberg States: O<sub>3</sub> and N<sub>2</sub>O Production," in preparation.

In addition, results from this work have been presented at the following conferences.

- C. G. Bressler, M. J. Dyer, and R. A. Copeland, "Wavelength Dependent Photogeneration of Ozone in Oxygen Matrices," 2nd International Conference on Low Temperature Chemistry, Kansas City, Missouri, August, 1996.
- C. G. Bressler, B. T. Schwartz, and R. A. Copeland, "Using Low Temperature Matrices to Study Reactions of the O<sub>2</sub> Herzberg States" 1996 Fall Meeting of the American Geophysical Union, San Francisco, California, December, 1996. [Eos, Trans. Amer. Geophys. Union 77, No. 46, F534 (1996)]
- 3. C. G. Bressler, M. J. Dyer, and R. A. Copeland, "Photogeneration and Spectroscopy of Ozone Monomers and Dimers in Oxygen Matrices," 44th Annual Western Spectroscopy Association Conference, Asilomar, California, January, 1997.
- C. G. Bressler, M. J. Dyer, and R. A. Copeland, "Photogeneration and Spectroscopy of Ozone Monomers and Dimers in Oxygen Matrices," 213th National ACS Meeting, San Francisco, California, April, 1997.
- C. G. Bressler and R. A. Copeland, "Temperature Dependence of the Infrared Spectroscopy of O<sub>3</sub> in Solid O<sub>2</sub>," 52nd International Symposium on Molecular Spectroscopy, Columbus, Ohio, June, 1997.

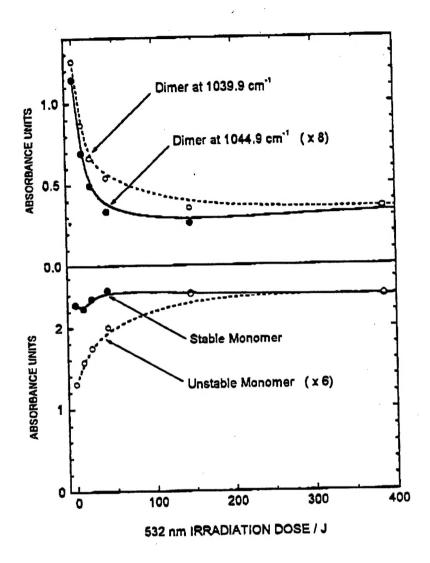


Figure 6. Concentration of O<sub>3</sub> monomers and dimers in an O<sub>3</sub> doped O<sub>2</sub> matrix (concentration 50: 1) as a function of exposure to 532 nm picosecond light.

Poster and oral presentations describing the results of the project were made at the AFOSR HEDM contractors meetings.

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